

COLLISIONALLY-MEDIATED SINGLET-TRIPLET CROSSING IN \tilde{a}^1A_1 CH₂ REVISITED: (010) COUPLING

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Methylene, CH₂, possesses a ground \tilde{X}^3B_1 ground electronic state and an excited \tilde{a}^1A_1 state only 3150cm⁻¹ higher in energy. The collision-induced singlet-triplet crossing in the gaseous mixtures is important in determining overall reaction rates and chemical behavior. Accidental near-degeneracies between rotational levels of the singlet state and the vibrationally excited triplet state result in a few gateway rotational levels that mediate collision-induced intersystem crossing. The mixed states can be recognized and quantified by deperturbation, knowing the zero-order singlet and triplet energy levels. Hyperfine structure can be used as alternative indicator of singlet-triplet mixing. Non-zero mixing will induce hyperfine splittings intermediate between the unresolved hyperfine structure of pure singlet and the resolvable (≈ 50 MHz) splittings of pure triplet, arising from the (**I**·**S**) interaction in the ortho states, where nuclear spin $I=1$ ^b. Collision-induced intersystem crossing rates from the (010) state are comparable to those for (000)^c, yet the identities and characters of the presumed gateway states are unknown. A new spectrometer is under construction to investigate triplet mixing rotational levels of $\tilde{a}^1A_1(010)$ by sub-Doppler measurements of perturbation-induced hyperfine splittings. Their observation will permit the identification of gateway states and quantification of the degree of triplet contamination of the singlet wavefunction. Progress in the measurements and the analysis of rotational energy transfer in (010) will be reported.

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